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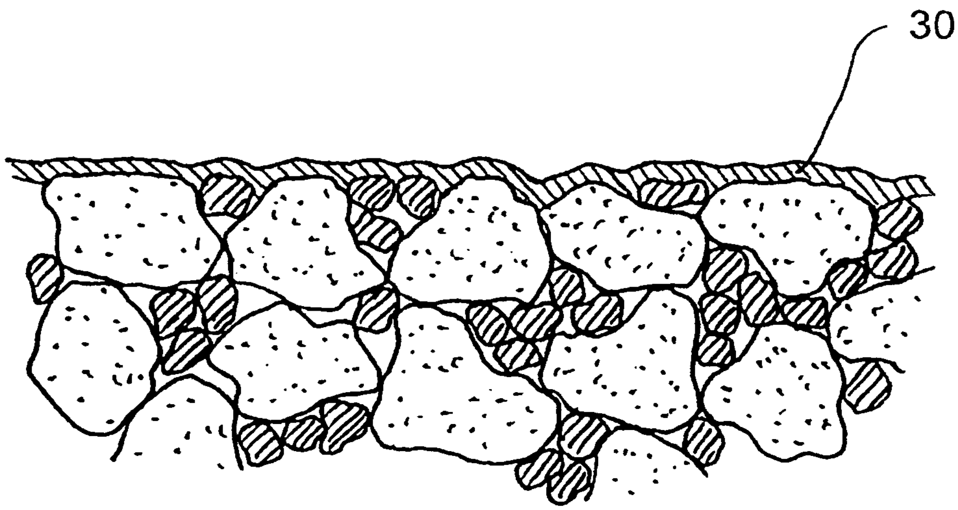
(54) Title: PROCESS FOR THE PRODUCTION OF EVAPORABLE GETTER DEVICES WITH REDUCED PARTICLE LOSS

(57) Abstract

A process for the production of barium-based evaporable getter devices with reduced particle loss is described, comprising the coating of the free surface (13) of the powder package (12) of the device with a vitreous layer (30) obtained by ultrasonic atomization of a solution of precursors of the layer forming glass.



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"PROCESS FOR THE PRODUCTION OF EVAPORABLE GETTER DEVICES WITH REDUCED PARTICLE LOSS"

The present invention relates to a process for the production of evaporable getter devices with a reduced particle loss.

As it is known, evaporable getter devices are employed in cathode-ray tubes, which form television screens, in order to allow the necessary vacuum level inside the tubes to be preserved during the expected tube life, which is of about 15 years.

Evaporable getter devices consist of an upperly open container, generally made of steel, which contains a compressed powder package, generally consisting of a mixture of powders of a barium and aluminum compound, $BaAl_4$, and of nickel. After having evacuated and sealed the picture tube, the getter device, previously introduced therein, is heated by induction from the outside, causing barium to evaporate and to deposit as a thin layer onto the tube internal walls; this metallic layer is the active material for the vacuum preservation, chemically binding the traces of gases which could outgas inside the tube during its life. In certain cases to the $BaAl_4$ and nickel powder mixture also powders of a nitrogenous iron or germanium compound are added, which releases nitrogen just before barium evaporation, thus increasing the extension and porosity of the metal deposit.

Barium-based evaporable getter devices are disclosed in many patents, such as US 3.558.962, US 4.077.899, US 4.342.662, US 5.118.988 and in the Japanese patent publication Hei 2-6185.

A problem occurring sometimes with the known devices is the loss of particles. As aforesaid, evaporable getter devices contain a package of powders which are compressed into the container by means of special shaped punches, but the powder particles at the free surface of the package (especially near to the container walls) can result poorly bound to the remaining part of the package; as a consequence a possible loss of powders from the getter device is experienced during the tube movement in the production line, before barium evaporation. The lost particles could locate on the grid provided inside the tube next to the screen

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internal wall, causing the presence of black spots in the image. This phenomenon is unacceptable for good quality television screens, and if found during the tube testing, this must be reopened, cleared of the barium compounds formed by air exposure of the metal, and submitted again to the process steps of introducing the getter device and following ones.

Object of the present invention is providing a process for the production of evaporable getter devices with reduced particle loss.

This object is obtained according to the present invention by a process of production of evaporable getter devices comprising the following steps:

- production, according to known methods, of a getter device formed of an upperly open metal container which contains a powder package of a mixture of $BaAl_4$, nickel and, possibly, a nitrogenous iron or germanium compound;

- ultrasonic atomization of an alcoholic solution of at least one glass precursor compound on the free surface of the powder package;

- formation of a vitreous layer on the free surface of the powder package by evaporating the solution solvent and subsequently thermally treating the getter device at a temperature in the range of about 250°C to 350°C under vacuum.

Object of the invention is also that of providing an evaporable getter device produced according to such a process.

The invention will be disclosed in the following with reference to one preferred embodiment, given as a non-limiting example, with reference to the drawings, wherein:

- Fig. 1 shows one possible kind of evaporable getter device;

- Fig. 2 shows a portion of the powder package of an evaporable getter device which is not coated with a vitreous layer according to the invention;

- Fig. 3 shows a portion of the powder package of an evaporable getter device coated with a vitreous layer according to the invention.

An evaporable getter device 10, corresponding to the geometry which is mostly employed, is shown in Fig. 1; this kind of device is composed of a container 11 shaped as a ring channel with an essentially rectangular cross-section, inside which a powder package 12, whose upper surface 13 is free, is provided.

Fig. 2 shows a detail of the powder package, made of $BaAl_4$ powder 20 and nickel powder 21, the particle size of the latter being generally thinner; the nitrogenous compound, whose presence is optional, is not shown. The upper surface 13 of the powder package is out of contact with the container walls. Although Fig. 1 shows a particular kind of getter device, in practice the invention process can be applied to all known evaporable getter devices. As far as the description of the various kinds of evaporable getter devices and of their preparation is concerned, reference is made to the aforementioned patents.

The process of the invention produces the result of stabilizing mechanically, by means of a thin vitreous layer, the free surface of the powder package which is obtained by compression of the mixture of $BaAl_4$, nickel and, possibly, nitrogenous compound; Fig. 3 shows the same powder package portion of Fig. 2, this time coated with the vitreous layer 30.

After having produced an evaporable getter device according to a known method, the process of the invention comprises atomization of an alcoholic solution of at least one compound precursor of a glass on the free surface 13 of the powder package by ultrasonic atomization.

The alcoholic solution is prepared according to methods and rules typical of the sol-gel technique. The vitreous layer 30 which is obtained at the end of the process is generally made up of a mixed oxide comprising a first component selected from silicon oxide, SiO_2, germanium oxide, GeO_2, or mixtures thereof, and boron oxide, B_2O_3, as a second component; the molar ratio between the first and the second component is generally included between 1:3 and 3:1, and preferably about 1:1. It is also possible to add little amounts of other oxides, such as aluminum oxide, in percentages generally lower than 10% referred to the glass composition. Preferred for this application is the use of equimolar mixtures of silicon oxide and boron oxide. Alcoholates are generally used as precursor for the oxides, such as silicon tetramethylate, $Si(OCH_3)_4$, silicon tetraethylate, $Si(OCH_2\text{-}CH_3)_4$, germanium tetraethylate, $Ge(OCH_2\text{-}CH_3)_4$, boron triethylate, $B(OCH_2\text{-}CH_3)_3$ and aluminum triisopropylate, $Al(OCH\text{-}(CH_3)_2)_3$. The use of ethylates is preferred. The solvent generally contains methyl or ethyl alcohol, with

preference for the latter because of the toxicity of the former.

Addition of at least two water moles per mole of precursor is always requested for the vitreous layer formation, in order to carry out the precursor hydrolysis and condensation reactions, described in the following. Generally, about 0.01 moles of nitric acid per mole of precursor are further added, in order to enhance the rate of the reactions which lead to the vitreous layer formation. The solution concentration is generally comprised in the range of about 2 to 20 grams of precursor compounds per liter of solution.

The resulting solution is atomized on the free surface 13 of the powder package of the mixture of $BaAl_4$, nickel and, possibly, nitrogenous compound by ultrasonic atomization.

Getter devices having the powder free surface coated with a thin vitreous layer are already known, for instance from the previously mentioned patent US. 4, 342, 662 and Japanese patent publication Hei 2-6185. These documents disclose coating methods such as dipping the getter device in the solution of the precursors, or the "spin-coating", which consists in placing one solution drop on the surface that has to be coated and spinning fast the getter device about its axis, in order to spread uniformly the solution on the whole powder surface. However, these methods allow a relatively thick vitreous layer to be obtained, with a waste of material and a possible effect of barium evaporation delay. Alternatively, the coating could be carried out by the conventional atomization, wherein the solution is either forced through the spraying nozzle by a gas pressure (generally air or nitrogen) in the solution tank, or is sucked by the depression created in the zone of the nozzle by a high gas flow; in both cases, however, the atomization flow rate is very high, resulting again in thick final vitreous layers. Besides, with these techniques the atomization cone is relatively broad, generally covering a surface which is wider than that of the powders, a vitreous deposit being thus obtained at the end of the process also on the powder container, what is undesired by electronic tubes manufacturers.

The process of the invention, on the contrary, makes use of ultrasonic atomization. The method consists in causing the vibration at ultrasonic frequency

of the free surface of the liquid which is about to pass through the spraying nozzle; with increasing of the ultrasound supplied energy, the vibration amplitude increases, and so does the distance between crests and depths of the liquid surface, until the vibration amplitude is such that the surface breaks, forming liquid droplets at the crests. This technique allows for two main advantages to be obtained, compared with the conventional atomization techniques. First, very low liquid flow rates, even of few μl per second, can be obtained. Then, the atomized product is delivered as a collimated beam, instead of a wide conical one; for instance, areas coated with the atomized product having a diameter of 1 mm or even less can be obtained, as well as, directing gas flows towards the atomized product, this can be defocused, thus obtaining atomized cones allowing the uniform coating of areas having a diameter of up to 50 cm. The combination of these two characteristics allows a precise coating of the powder surface only with a very small amount of solution, giving rise to an extremely low thickness of the final vitreous layer.

Ultrasonic atomizers are widespread on the market and sold for instance under the name AccuMist™ of the company Sono-Tek Cop., Milton, NY, USA; the technical -commercial handbook of these atomizers reports details on principle and procedures of their operation.

The atomization according to the invention is carried out with a flow rate of the solution of precursors in the range of about 10 to 50 μl/second. The distance between spraying nozzle and the powder surface to be coated is generally in the range of 0.5 to 5 cm.

Once the powder free surface 13 has been coated with the solution of precursors, the vitreous layer 30 is formed by evaporation of the solution solvent and reaction among the molecules of the glass precursor compound.

The occurring chemical reactions are:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + n\ ROH \qquad (I)$$

$$M(OH)_n + M'(OH)_m \rightarrow (OH)_{n-1}M\text{-}O\text{-}M'(OH)_{m-1} + H_2O \qquad (II)$$

wherein:

M and M', being the same or different, are elements whose oxide is intended

to form the vitreous layer;

n and m are the valence numbers of M and M', respectively; and

-OR is the alcoxide radical corresponding to the ROH alcohol.

The reaction (I), precursor hydrolysis, requires at least 2 water moles per precursor mole. Preferably, according to the present invention, the least amount possible of water is employed, the molar ratios between this and the total sum of precursor moles being in the vicinity of 2, since water could react with the $BaAl_4$ compound, modifying the characteristics thereof. Water is here a reagent and is preferably added at the end of the solution preparation, or rather just before atomization, in order to avoid the solution to become exceedingly viscous and unsuitable to atomization as a result of the progress of the reactions (I) and (II). Reaction (II) proceeds until all the -OH groups have reacted with elimination of one water molecule and formation of an oxygen bridge between two different atoms (condensation reaction). Since the M and M' elements which are employed are at least trivalent, a tridimensional lattice of M and M' atoms, bound to each other by oxygen bridges, which constitutes the final glass structure, is formed in this way.

Considering the destination of use of the getter devices, the steps following the solution atomization are carried out under vacuum, in order to minimize entrapping of atmospheric gases in the vitreous film 30 or in the interstices between the powder particles 20, 21 which form the package 12. Further, operating under vacuum enhances reactions (I) and (II), because of the continuous removal of the ROH alcohol, which is formed in reaction (I) and of the water which is formed in reaction (II).

The last step is the consolidation of the vitreous layer formed in the reaction (II), which is carried out by operating, still under vacuum, at a temperature in the range of about 250 and 350 °C.

The invention will be further illustrated by the following examples. These non-limiting examples illustrate some embodiments intended to teach those skilled in the art how to put the invention into practice, and intended to represent the considered best way to carry out the invention.

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EXAMPLE 1

25 evaporable getter devices of the kind exemplified in Fig. 1 are produced. Each getter device has an external diameter of 20 mm, and a width of the powder containing channel of about 6 mm, and contains 1000 mg of a mixture of 1:1 weight ratio of $BaAl_4$, having a particle size lower than 250 μm, and nickel, having an average particle size of about 10 μm; the powders are compressed in the container by applying a pressure of about 3000 kg/cm^2 to the compressing punch. The 25 resulting getter devices are coated by ultrasonic atomization with a solution obtained by adding 2.1 grams of silicon tetraethylate and 2.9 grams of boron triethylate to 1 liter of ethyl alcohol. 90 ml of bidistilled water are added to such a solution just before atomization. The solution is atomized by operating with a nozzle that, kept at a distance of about 1 cm from the powder surface, defines on this surface an atomization zone of about 0,3 cm^2; the solution is atomized with a flow rate of about 30 μl/sec, while shifting the nozzle on the surface of the powder package with a linear rate of about 4.4 cm/second, so that the complete coating takes about one second; the amount of solution atomized on the powder surface is about 0.15 μl/cm^2. Subsequently, the getter devices coated in this way are placed into a furnace which is kept under suction, brought in 90 minutes to the temperature of 350°C and then withdrawn from the furnace.

EXAMPLE 2

The 25 samples prepared as described in Example 1 are subjected to a particle loss test. A beaker is prepared, on the bottom of which a metallic filter is laid, having porosity of 0.65 μm, whose weight is known with a precision of ± 0.1 mg. The beaker is filled with FORANE ® 141b DGX, sold by the company ELF ATOCHEM ITALIA, Milano, composed by 1,1-dichloro-1-fluoroethane containing little amounts of a stabilizing compound. The samples are introduced in the liquid one by one and subjected to ultrasonic vibration for two minutes. At the end of the test the filter on the bottom of the glass is withdrawn, heated for 5 minutes by an infrared lamp for evaporating the FORANE® and weighed: the weight increase with respect to the initial weight is divided by the number of samples, producing thus the average weight loss per sample. In the present test the

obtained average value of weight loss was 0.37 mg per sample.

EXAMPLE 3 (COMPARATIVE)

The test of Example 2 is repeated with 25 getter devices prepared as described in Example 1, but not coated with a vitreous layer by ultrasonic atomization. The average weight loss per sample was 0.56 mg.

The comparison between the results of Examples 2 and 3 shows that the samples coated according to the process of the invention have an average value of lost particles weight which is reduced of about 35% compared to evaporable getter devices prepared according to the best manufacturing techniques used in this field but not coated with the vitreous layer.

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CLAIMS

1. – A process for the production of evaporable getter devices (10) with reduced particle loss, comprising the following steps:
   - production, according to known methods, of a getter device formed of an upperly open metallic container (11), which contains a powder package (12) of a mixture of $BaAl_4$ (20), nickel (21), and, possibly, a nitrogenous iron or germanium compound;
   - ultrasonic atomization of an alcoholic solution of at least one glass precursor compound on the free surface (13) of the powder package;
   - formation of a vitreous layer (30) on the free surface of the powder package by evaporating the solution solvent and subsequently thermally treating the getter device at a temperature in the range of about 250 to 350 °C under vacuum.
2. A process according to claim 1 wherein the solution to be atomized is prepared using an alcohol as solvent, one or more compounds selected from silicon tetramethylate, silicon tetraethylate, germanium tetraethylate, boron triethylate and aluminum triisopropylate as glass precursor and adding at least 2 moles of water per mole of precursor.
3. A process according to claim 2 wherein the precursor is silicon tetraethylate, the alcohol is ethyl alcohol and the concentration of the precursor is in the range of 2 to 20 grams of precursor compound per liter of solution.
4. A process according to claim 1 wherein atomization is carried out with a solution flow rate in the range of 10 to 50 μl/second.
5. A process according to claim 1 wherein the distance between spraying nozzle and the powder surface to be coated is in the range of 0.5 to 5 cm.
6. An evaporable getter device (10) with reduced particle loss produced according to the process of claim 1.

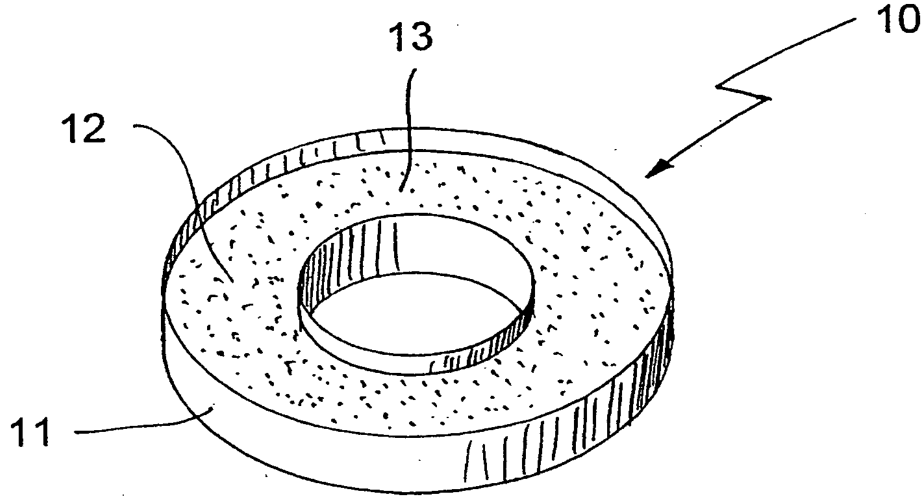

Fig. 1

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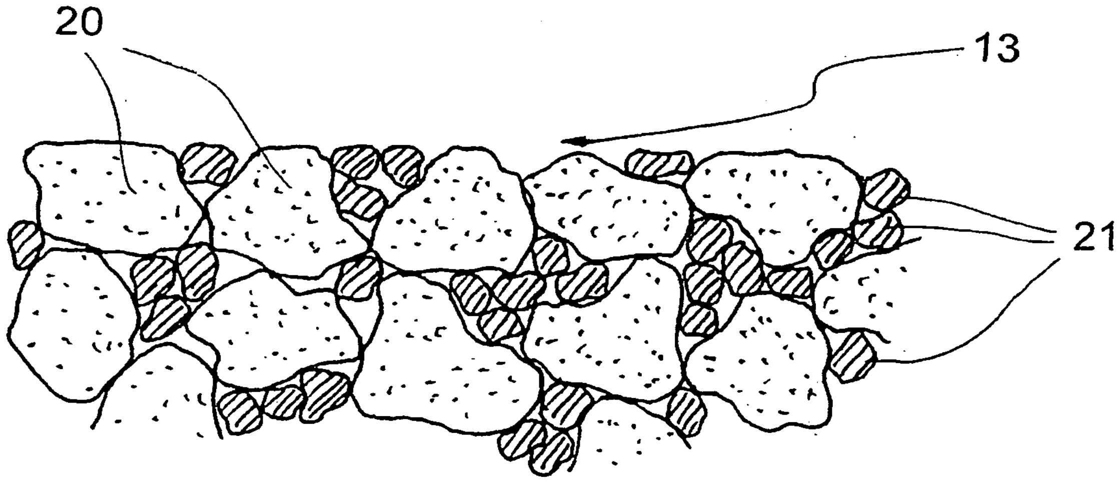

Fig. 2

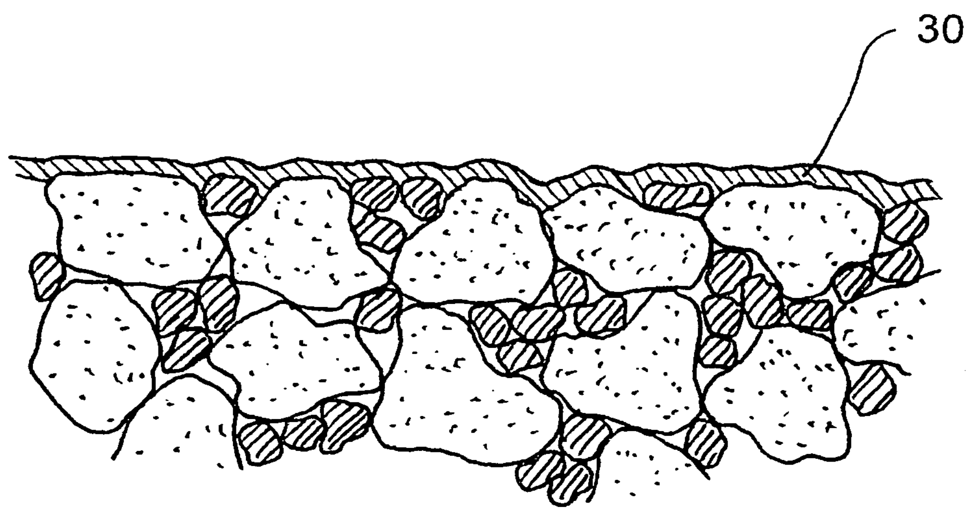

Fig. 3

INTERNATIONAL SEARCH REPORT

Interr nal Application No
PCT/IT 99/00233

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01J7/18 H01J29/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 028 372 A (TOKYO SHIBAURA ELECTRIC CO) 13 May 1981 (1981-05-13) cited in the application page 1, line 2 - line 6 claims 1-4 page 2, line 1 - line 11 page 3, line 10 - line 26 page 4, line 16 - line 25	6
A		1

A	GB 1 572 000 A (GETTERS SPA) 23 July 1980 (1980-07-23) page 1, line 6 - line 17 page 2, line 36 - line 48	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Intern nal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

.ormation on patent family members

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